and Br^- in a 1 *F* sodium bromide–1 *F* sodium nitrate medium, but a quantitative correlation is impossible.

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Vibrational Spectra of BrO^-, BrO_2^-, Br_3^-, and Br_5^-

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Vibrational spectra (laser-excited Raman and infrared) for the bromite and hypobromite ions in aqueous solution were obtained. Bond-stretching force constants were calculated and these, taken with published data for BrO_3^- and the ClO_n^- (n = 1, 2, or 3) series, indicate that the chemical-bonding changes in these two series are similar. If the observed increase in bond strength with increase in n is due to increasing p–d π bonding, it appears that 2p–4d π bonding in BrO_n^- is as effective as 2p–3d π bonding is in ClO_n^-. A proposed explanation for the instability of BrO_4^- assumes that this is not the case. Spectral features additional to those assigned to the oxyanions were observed under certain conditions; these were assigned to Br_3^- and Br_5^-.

Introduction

With the exception of perbromates, salts of the oxyacids of bromine have been known and used for many years,[1] but vibrational spectroscopic studies of the series have apparently been confined to the bromate ion. The present study was aimed at obtaining vibrational data for the remaining known ions in this series, the bromite and the hypobromite ions; the fundamental modes of these were assigned. In addition, under certain conditions, low-frequency Raman bands which were partly but not entirely assignable to Br_3^- were observed. The study was, for this reason, extended to include solutions of Br_2 and Br^- in several different solvents; the presence of Br_5^- was invoked to explain the additional spectral features.

Experimental Section

Raman spectra of solution and solid samples were obtained using a Perkin-Elmer LR1 photoelectric-recording instrument equipped with a Spectra-Physics 125 helium–neon laser emitting approximately 70 mw at 6328 A; polarization measurements were made using a half-wave, retardation-plate polarizer mounted in the laser beam, and instrumental polarization corrections were determined by making measurements with bands of known depolarization ratios. Infrared measurements were made using Beckman IR9 and IR11 instruments. Purified Br_2 (Dow), reagent grade NaOH, KOH, $Ba(OH)_2$, and KBr, and fractionally distilled acetonitrile, methanol, and propanol were used. Published procedures[2] were followed in the preparation of OBr^- and BrO_2^- solutions and of solid $NaBrO_2$.

Results

Figures 1 to 5 illustrate the spectra while Table I summarizes the frequency assignments. Within experimental uncertainty of approximately ±2 cm^{-1}, no differences in frequency were observed between spectra of solutions containing different cations and the mean values are quoted. The oxyanion solutions were yellow and, with the 6328-A exciting frequency, there was no absorption to produce distortion of the Raman spectrum; solutions of the tribromide and pentabromide were deep red and some distortion was inevitable. For the present qualitative purposes this absorption is not a significant deficiency.

Discussion

a. **Hypobromite Ion.**—The initial reaction product of Br_2 and OH^- at 0° is the hypobromite ion; Figure 1 illustrates a typical Raman spectrum. The strong, polarized band at 620 cm^{-1} is the fundamental mode of the diatomic BrO^-. It was accompanied by a polarized band of variable relative intensity at 807 cm^{-1} (BrO_3^-) and, on occasion, by a polarized band at 709 cm^{-1} (BrO_2^-). These assignments are based on the spectral changes observed as the reaction was carried further through the BrO_2^- stage to the final product, BrO_3^-; earlier studies[3] had established the four fundamental modes of BrO_3^-.

When excess Br_2 was added, the BrO^- band disappeared, the BrO_3^- band at 806 cm^{-1} was enhanced, and three overlapping, polarized bands appeared in the region below 300 cm^{-1} (Figure 1). These three bands are assigned to the interaction products of Br_2 and Br^-; the latter is a product of the main reaction

$$Br_2 + 2OH^- \longrightarrow BrO^- + Br^- + H_2O$$

and, with excess Br_2 present

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

and

$$Br_2 + Br_3^- \rightleftharpoons Br_5^-$$

may occur.

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[1] A recent review of this topic which contains a comprehensive bibliography follows: Z. E. Jolles, Ed., "Bromine and its Compounds," Academic Press Inc., New York, N. Y., 1966.

[2] See ref 1, pp 155, 160.

[3] J. H. Hibben, "The Raman Effect and its Chemical Applications," ACS Monograph No. 80, 1939, p 439.

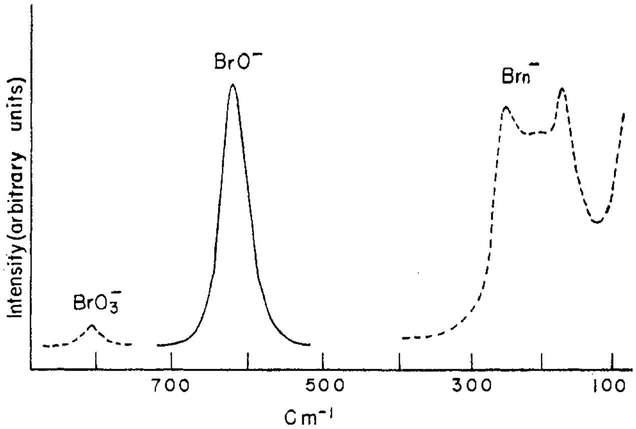

Figure 1.—Raman spectra of the reaction products of Br_2 and OH^-: (a) full line shows spectrum of initial product, BrO^-, formed when OH^- is in excess: 6.8 M OH^- with 2.1 M Br_2; (b) dotted line shows spectrum when Br_2 is added in excess.

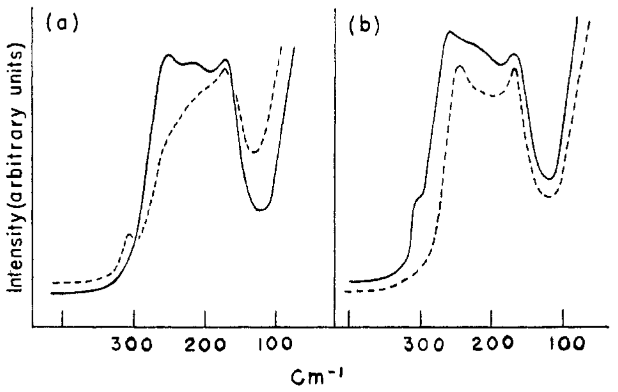

Figure 2.—Raman spectra of aqueous solutions of Br_2 and KBr: (a) effect of dilution at constant Br_2/Br^- ratio: full line is the spectrum of a solution of 1 M KBr and 1 M Br_2; dotted line is the spectrum of a solution of 0.25 M KBr and 0.25 M Br_2; (b) effect of changing Br_2/Br^- ratio: full line is the spectrum of solution with 0.67 M Br_2 and 0.34 M KBr; dotted line is that of 0.67 M Br_2 and 6.8 M KBr solution.

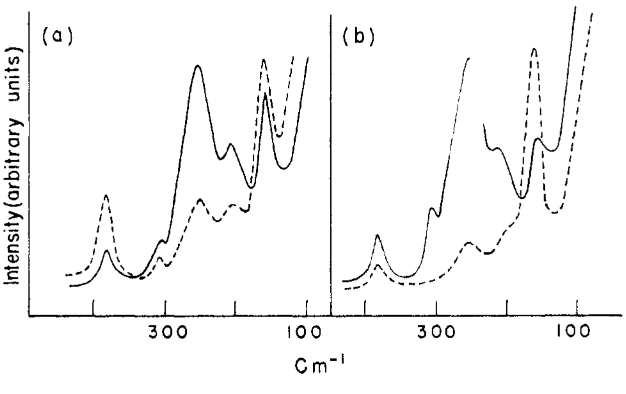

Figure 3.—Raman spectra of acetonitrile solutions of Br_2 and KBr: (a) effect of dilution at constant Br_2/Br^- ratio: full line is the spectrum of a solution of 0.69 M Br_2 and 0.32 M KBr; dotted line is that of a solution of 0.17 M Br_2 and 0.08 M KBr; (b) effect of changing Br_2/Br^- ratio: full line is the spectrum of a solution of 0.69 M Br_2 and 0.16 M KBr; dotted line is that of a 0.36 M Br_2 and 0.36 M KBr solution.

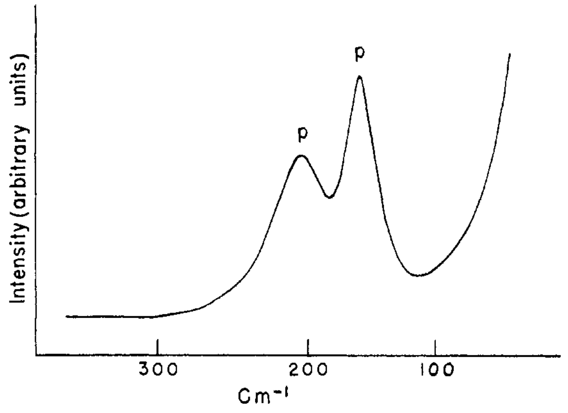

Figure 4.—Raman spectrum of an approximately 1 M solution of Br_2 in n-propyl alcohol.

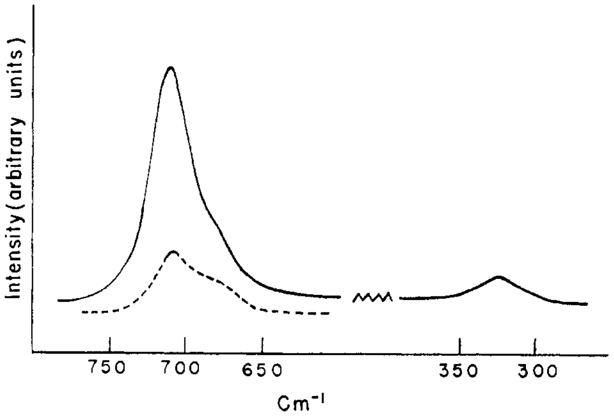

Figure 5.—Raman spectrum of an approximately 1 M aqueous solution of sodium bromite: full line is the spectrum obtained with incident light polarized perpendicularly to the direction of observation; dotted line is that with light vector rotated through 90°.

Table I

Collected Raman Wavenumber Values[a] for BrO^-, BrO_2^-, Br_3^-, and Br_5^-

Ion	Wavenumber,[b] cm⁻¹ Aqueous soln	CH₃CN	n-C₃H₇OH	Solid
BrO^-	620 (0.4)[c]			
BrO_2^-	709 (0.3)			700 anhyd $\left\{\begin{matrix}728\\680\end{matrix}\right.$
	680 (Dp)			
	324 (Dp)			~330
Br_3^-	170 (0.4)	163 (0.4)	160 (0.4)	
	~210	~205 (~0.7)	201 (0.5)	
Br_5^-	250 (0.4)	257 (0.4)		

[a] Fewer infrared data were obtained; these are mentioned in the text. [b] Values quoted carry an uncertainty of about ±2 cm⁻¹ except for overlapping bands for which the uncertainty is larger. [c] Values in parentheses are depolarization ratios; Dp = depolarized.

b. Br_3^- and Br_5^-.—The two bond-stretching fundamental modes of Br_3^- were assigned to bands near 160 and 190 cm⁻¹ by Person and co-workers[4] on the basis of Raman and infrared studies in several solvents. The third Raman band in this region, near 250 cm⁻¹, which was observed by these authors only in aqueous solution, was suggested to arise from free halogen complexed with a strong donor available in the solution; presumably, this implies the Br_5^- complex ion. Attempts were made to vary the relative band intensities of the overlapping triplet by dilution (Figure 2a) and by preparing aqueous solutions of KBr and Br_2 with

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(4) W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, **35**, 908 (1961).

different Br^-/Br_2 ratios (Figure 2b). Some success was achieved in showing that the band near 250 cm^{-1} behaved as would be expected for Br_5^-. Dilution reduced its intensity relative to that of the Br_3^- ν_1 band near 170 cm^{-1}; the new feature observed near 300 cm^{-1} upon dilution is the fundamental band of Br_2. A higher Br_2/Br^- ratio enhanced the intensity of the 250-cm^{-1} band relative to that of Br_3^-, but this was not very marked and other solvents were examined in the hope that larger changes could be produced. Acetonitrile was suitable; see Figure 3. All bands were sharper in this solvent and it was possible to attain readily solutions in which there was little Br_5^- and also the other extreme in which the Br_5^- band dominated the spectrum (Figure 3b). Dilution at a constant Br^-/Br_2 ratio again also supported the interpretation; see Figure 3a.

With methanol as solvent the addition of only Br_2 gave spectra which were time dependent; the Br_2 band decreased while the Br_3^- bands increased and then gave way to the Br_5^- band. Slow oxidation of the solvent and production of Br^- accounts for these observations. With *n*-propyl alcohol the reaction was faster and a spectrum showing only Br_3^-, Figure 4, was obtained. In contrast to the corresponding spectrum in acetonitrile the band near 190 cm^{-1} assigned to ν_3, the antisymmetric stretching mode of Br_3^-, was very prominent and its depolarization could be measured; it was polarized to about the same extent (0.5) as the band assigned to ν_1. This suggests that Br_3^- is linear but not symmetrical in propanol solution. In aqueous solution, overlapping of bands prohibits a meaningful measurement of the depolarization ratio of the ν_3 band but its appreciable intensity indicates some departure from the linear, symmetric configuration. In acetonitrile solution in which anion–solvent interaction would be expected to be less significant and in which cation–solvent interaction should take care of the perturbing influence of the cation, the anion spectrum indicates the least perturbation.

Nothing conclusive can be said about Br_5^- on the basis of one polarized Raman band only; neither it nor any other band assignable to Br_5^- was observed in the infrared spectrum of the solution which gave the full-line Raman spectrum in Figure 3b. The band frequency and the indication that other vibrational modes are of considerably lower frequency do, however, suggest that Br_5^- is not merely a loose $Br_2 \cdot Br_3^-$ complex but is a more symmetric species approximated better by $[Br_2 \cdot Br \cdot Br_2]^-$ in which the two outer bonds are considerably stronger than the two inner bonds. The configuration need not be a linear one and by analogy with the known I_5^- ion a preferable choice would be the L shape.[5] This is analogous to the earlier conclusion reached for the Cl_5^- ion.[6]

c. Bromite Ion.—Under suitable conditions[2] the hypobromite ion may disproportionate to the bromite and bromide ions without excessive conversion to the bromate. Several such preparations were made with varying degrees of success using sodium, potassium, and barium hydroxides. Most successful was the sodium bromite preparation, and Figure 5 illustrates the Raman spectrum; some bromate was present. Other preparations showed varying amounts of hypobromite in addition to the bromate and bromite. Three Raman bands were observed for the bromite ion; one, the most intense, at 709 cm^{-1} was polarized while the other two were apparently depolarized. One of these was a shoulder, at 680 cm^{-1}, on the side of the strong, polarized band while the other was at 324 cm^{-1}. These observations are compatible with the expected structure of C_{2v} symmetry which requires three Raman-active modes, two of which may yield polarized bands. ν_1, the symmetric stretching mode, is assigned to 709 cm^{-1}, ν_2, the bending mode, to 324 cm^{-1}, and ν_3, the antisymmetric stretching mode, to the 680-cm^{-1} band. Aqueous solutions, supported between silver bromide, gave infrared spectra which, although not of good quality because of the broad water absorption in this region, also indicated the presence of two bands near 700 cm^{-1}. Solid $NaBrO_2 \cdot 3H_2O$ showed two Raman bands of almost equal intensity near 700 cm^{-1}, at 728 and 680 cm^{-1}, but on dehydration to $NaBrO_2$ these were replaced by a single band at 700 cm^{-1}. Nujol mulls of these solids showed corresponding bands in the infrared spectra. All are assigned to ν_1 and there was no definite feature assignable to ν_3 in the solid spectra; presumably it is obscured beneath the stronger ν_1 bands. ν_2 was detected in the Raman spectrum of solid $NaBrO_2$ and a weak and barely discernible infrared band was found in the same region.

d. Force Constants.—A simple valence-force field calculation for the BrO_2^- ion,[7] made with an assumed value of 110° for the OBrO angle, yielded $k_{BrO} = 4.2$ mdynes/A; for BrO^-, $k_{BrO} = 3.0$ mdynes/A. The corresponding k_{ClO} values are: $k_{ClO}(ClO_2^-) = 4.35$ mdynes/A[8] and $k_{ClO}(ClO^-) = 3.3$ mdynes/A,[9] while the simple valence-force field values for the chlorate and bromate ions are 5.7 and 5.2 mdynes/A, respectively.[10] Thus, a nearly linear correlation exists between k_{ClO} and k_{BrO} for the three lower member pairs of the XO_n^- series. This implies that the changes in the bonding within these two series are analogous and gives no inkling that the next member of the BrO_n^- series, BrO_4^-, is so unstable that its existence has not been demonstrated.

The importance of π bonding between the chlorine 3d orbitals and the oxygen 2p orbitals in ClO_n^- ions has been emphasized repeatedly;[11-14] the progressive

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[5] J. Broekema, E. E. Havinga, and E. H. Weibenga, *Acta Cryst.*, **10**, 596 (1957).

[6] J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44**, 3638 (1966).

[7] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y. 1945, p 168.

[8] J. P. Mathieu, *Compt. Rend.*, **234**, 2272 (1952).

[9] G. Kujumzelis, *Z. Physik*, **39**, 665 (1938).

[10] K. W. F. Kohlrausch, "Ramanspektren," Akademie-Verlagsgesellschaft Becker-Erler, Leipzig, 1943, p 135.

[11] L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948, p 239.

[12] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[13] E. L. Wagner, *J. Chem. Phys.*, **37**, 751 (1962).

[14] D. S. Urch, *J. Inorg. Nucl. Chem.*, **25**, 771 (1963).

shortening of the Cl–O bond in the series ClO_2^-, ClO_3^-, and ClO_4^- [12] and the increasing Cl–O stretching force constant[13] have been attributed to the increasing π bonding. Comparable bond-length data are not available for the BrO_n^- series. In an attempt to explain the instability of BrO_4^-, Urch[14] has attempted to calculate the relative efficiencies of the chlorine 3d and the bromine 4d orbitals in their π bonding with oxygen 2p orbitals and has concluded that the 4d orbitals are much less efficient. Since the tetrahedral σ-bond frameworks for these XO_4^- ions are similar and weak, because the 3s and 4s electrons are tightly bound and cannot participate effectively, he further concludes that the absence of good π bonding in BrO_4^- explains its instability. The present correlation suggests, however, that, if increasing π bonding is the predominant factor in the ClO_n^- series, it is probably also this factor which predominates in producing the analogous changes in bond force constants in the BrO_n^- series; *i.e.*, 3d–2p and 4d–2p π bonding are not very different in efficiency, at least in the first three members of the series.

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Spectra of Uranium(IV) and Uranium(III) in Molten Fluoride Solvents[1]

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The spectra of U(IV) and U(III) in molten LiF–BeF_2, LiF–BeF_2–ZrF_4, and LiF–NaF–KF have been obtained at temperatures up to 540° over the wavelength range of 200 to 2400 nm. Based on a comparison of these spectra with those obtained in other molten salt systems and aqueous systems, it is suggested that the coordination number of the uranium species in the molten fluoride media studied is possibly 8 or 9. Clearly, these ions are not in the environment found in chloride melts. By chemical means, it was not possible to obtain a solution of U(III) which was free of U(IV). The reaction of U(III) with alkali fluorides, under the experimental conditions of the study, is also discussed.

Introduction

Spectrophotometry offers a rather straightforward approach to the determination of various oxidation states of uranium in molten fluoride salts provided the effect of various parameters on the spectra of these dissolved species is known. A study of the spectra of U(IV) and U(III) in several molten fluoride solvent systems was undertaken in order to gain knowledge about the environment of these solute species and compare this environment to that of other solvent systems. Earlier the partial spectrum of uranium(IV) in molten LiF–NaF–KF had been reported.[2] The work described here was carried out mainly in the solvent systems 2LiF–BeF_2 (66–34 mole %), LiF–BeF_2–ZrF_4 (66–29–5 mole %), and LiF–NaF–KF (46.5–11.5–42.0 mole %). Spectra of U(IV) and U(III) in various molten chloride solutions have been reported by Gruen and McBeth[3a] and by Morrey.[3b]

Experimental Section

These spectra were recorded by means of a Cary recording spectrophotometer, Model 14M. The molten LiF–NaF–KF samples were contained in 0.25-in. o.d. captive liquid cells[4] and the molten samples of the LiF–BeF_2 type were contained in modified captive liquid cells which had no "keeper holes."[4] As LiF–BeF_2-type melts are nonwetting, the keeper holes are unnecessary. In a further modification to reduce the volume of salt required, the optical apertures were located about $^1/_{32}$ in. above the bottom of the cell. The cells were made of copper or graphite for these studies. They were loaded with solid chunks of solidified salt solutions, chunks of solidified solvent, and solid UF_3 or UF_4 which would dissolve on melting, or with solvent and UF_4 plus a reducing agent such as uranium, zirconium, or beryllium metal. In all cases, the samples were loaded in an inert atmosphere box. Each loaded cell was placed in a vacuum-tight container for transfer to the heated cell assembly without exposure to the atmosphere as the transfer container served as the lid of the cell assembly. The cell is suspended[4] on a quartz rod, and the end of the rod protrudes through a Teflon ferrule in the top of the transfer container. After the cell assembly had been evacuated and filled with helium gas, a modified gate valve was opened in the bottom of the transfer container and the captive liquid cell and its contents were lowered and positioned within the cell assembly by manipulation of the portion of the quartz rod which was outside the furnace. Generally the cell assembly and its contents are baked under vacuum at 250° for 1 hr before helium is readmitted and the sample melted.

The samples were melted in a heated cell assembly similar in external appearance to the one described earlier[5] but modified internally so that the sample and cell are contained in a vacuum-tight helium atmosphere. The interior of the cell assembly consists of an inverted T-shaped nickel tube. Light from the spectrophotometer passes through the horizontal portion of the "T" which is welded to the exterior walls of the cell assembly. The vertical part is welded to the top of the assembly. Windows are sealed on the cooled ends of the horizontal tube as described before.[5] Ten rod-shaped heating elements are positioned outside the junction of the "T" but within a large mass of nickel which surrounds the junction; thus, the mass of heated metal provides more uniform heating than that of the original design. Further,

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] J. P. Young and J. C. White, *Anal. Chem.*, **32**, 799 (1960).

[3] (a) D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959); (b) J. R. Morrey, *Inorg. Chem.*, **2**, 163 (1963).

[4] J. P. Young, *Anal. Chem.*, **36**, 390 (1964).

[5] J. P. Young and J. C. White, *ibid.*, **31**, 1892 (1959).